Journal of Saudi Chemical Society (2016) **20**, 373–378

King Saud University

Journal of Saudi Chemical Society

www.ksu.edu.sa
www.sciencedirect.com

ORIGINAL ARTICLE

The effect of different molar ratios of ZnO on characterization and photocatalytic activity of TiO_2/ZnO nanocomposite

Shahram Moradi [a], **Parviz Aberoomand-Azar** [b], **Sanaz Raeis-Farshid** [a,*], **Saeed Abedini-Khorrami** [a], **Mohammad Hadi Givianrad** [b]

[a] *Department of Chemistry, Tehran North Branch, Islamic Azad University, Tehran, Iran*
[b] *Department of Chemistry, Science and Research Branch, Islamic Azad University, Tehran, Iran*

Received 3 May 2012; accepted 7 August 2012
Available online 19 August 2012

KEYWORDS

TiO_2/ZnO nanocomposite;
Decolorization;
Sol–Gel;
UV irradiation;
Methylene Blue

Abstract The TiO_2/ZnO nanocomposite as a photocatalyst was prepared with different molar ratios of ZnO using the sol–gel method. The structures and properties were recognized with Fourier transform infra-red spectroscopy (FT-IR), scanning electron microscopy (SEM), and X-ray diffraction (XRD) methods. The XRD study exhibited that the crystallization behavior of the nanocomposites was associated with the molar ratios of ZnO. The SEM images indicated that with increasing the molar ratio of TiO_2/ZnO until 50:10, regular morphology can be seen. It should be of interest for catalytic purposes since it expectantly improves the surface area. Furthermore, the photocatalytic activity of the synthesized nanocomposites was investigated for decolorization of Methylene blue (MB) in water under UV irradiation in a batch reactor. The results revealed that the photocatalytic activity of nanocomposite with 50:10 M ratio of TiO_2/ZnO was the best.

1. Introduction

One of the most important sources of environmental contamination is dye pollution. Textile's wastewater consists of these dyes, which many of them are azo compounds that can be satisfactorily removed by semiconductor photocatalysts (Weber and Stickney, 1993; Chen et al., 2008).

Recently, the use of semiconductor photocatalysts has been much noticeable to solve some environmental pollution. In the number of various semiconductors, which were used; titanium dioxide (TiO_2) was one of the most important photocatalyst for the degradation of environmental contaminants. This is because of its high photocatalytic activity, non-toxicity, chemical stability under different conditions, and relative inexpensiveness (Liqiang et al., 2004; Abdel Aal et al., 2008; Tian et al., 2009a, b). TiO_2 is an effective material for the degradation of dyes from wastewater. However, because of its large band gap (3.2 eV); it cannot absorb sunlight, successfully. To reduce the band

* Corresponding author. Tel.: +98 21 22262561; fax: +98 21 22222512.
E-mail address: S_R_Farshid@yahoo.com (S. Raeis-Farshid).
Peer review under responsibility of King Saud University.

ELSEVIER Production and hosting by Elsevier

http://dx.doi.org/10.1016/j.jscs.2012.08.002

gap and increase the photoactivity of TiO_2, various ways have been tested, which one of them is its doping with different metal ions and oxides (San et al., 2002; Siemon et al., 2002; Liao et al., 2004; Xie and Yuan, 2004; Chen et al., 2008). ZnO carries out this by increasing the charge separation and extending excitation energy range. Furthermore, the band gap energy of ZnO is much similar to that of TiO_2. Alternatively, ZnO is a main semiconductor for the synthesis of visible-light-active photocatalysts (San et al., 2002; Siemon et al., 2002; Khan et al., 2008; Khan and Kim, 2009; Tian et al., 2009a,b).

Some researchers have synthesized nanocomposite through various methods, including hydrolysis deposition, thermal chemical vapor deposition, radio frequency magnetron sputtering, spray pyrolysis, and sol–gel methods. The sol–gel process has significant advantages compared to other methods such as high purity, good uniformity of the microstructure of powder, synthesis at low temperature and easily controlled reaction conditions. Therefore this method has been used to prepare of TiO_2/ZnO nanocomposite (Miki-Yoshida et al., 2002; Kim et al., 2007; Zhang et al., 2007; Chung et al., 2008).

In this work, TiO_2/ZnO nanocomposite was prepared by sol gel method and characterized by means of X-ray diffraction (XRD), scanning electron microscopy (SEM), and Fourier transform infra-red spectroscopy (FT-IR). The photocatalytic activity of the synthesized nanocomposite was investigated for decolorization of Methylene Blue (MB) in water under UV irradiation in a batch reactor. The effect of zinc oxide molar ratio on the photocatalytic behavior of nanocomposite was studied in detail.

2. Experimental

2.1. Material and methods

The chemicals used in this study were tetra isopropyl orthotitanate (TTIP), zinc nitrate tetra hydrate, diethanolamine (DEA), glacial acetic acid, Methylene Blue (MB) and ethanol from Merck Chemical Company.

2.2. Preparation of nanocomposites

In this study, TiO_2/ZnO nanocomposite with different molar ratios of ZnO was prepared by the sol–gel process. The TiO_2 sol was made at room temperature, and TTIP was used as a precursor as follows: In the first stage, TTIP was dissolved in ethanol with a 1:9 M ratio of TTIP to ethanol and then was stirred for 15 min, to obtain a precursor solution. After that, a mixture of absolute ethanol, acetic acid, and deionized water with the molar ratio of 10:6:1 was added slowly into the precursor by a fast stirring and it was continuously stirred for 15 min to achieve a yellow transparent sol. Here, acetic acid was used as an inhibitor to reduce quick hydrolysis of TTIP, and so the pH value was adjusted to 5.

ZnO sol was prepared as follows: Firstly zinc nitrate tetra hydrate was dissolved in absolute ethanol with five different molar ratios, 0.1:110, 0.3:110, 0.5:110, 1:110, and 1.5:110. After that, stirred for 5 min, then a mixture of absolute ethanol, diethanolamine, and deionized water with the molar ratio of 10:2:1 was added slowly into the precursor by a fast stirring and it was continuously stirred for 15 min to achieve a transparent sol.

The prepared ZnO sol was directly added into the TiO_2 acidic sol with the molar ratio of 1:50, 3:50, 5:50, 10:50, and 15:50, to get TiO_2/ZnO sol. This sol aged for 24 h. After that, the prepared sol was dried in the air, then heat treated at 350 °C for 10 min and then at 500 °C for 5 h. The samples were naturally cooled after the heat treatment (Table 1) (Abdel Aal et al., 2008; Tian et al., 2009a,b; Weber and Stickney, 1993).

Table 1 Different TiO_2/ZnO molar ratios.

Sample	1	2	3	4	5	6
TiO_2/ZnO molar ratio	50:0	50:1	50:3	50:5	50:10	50:15

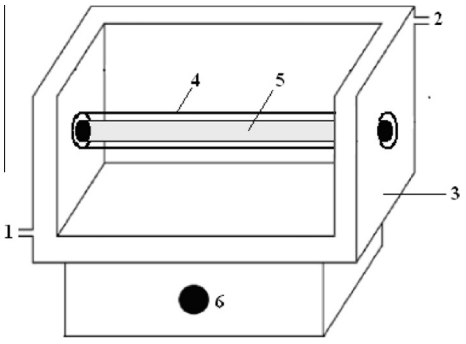

Figure 1 Schematic diagram of the photoreactor systems. (1) Water input, (2) water output, (3) glass jacket, (4) quartz cover, (5) UV lamp, (6) stirrer.

2.3. Characterization of nanocomposites

FT-IR spectra were obtained as KBr pellets in the wave number range of 4000–400 cm^{-1} using Thermo Nicolet Nexus 870 FT-IR spectroscopy. Phase identification of the nanocomposites was done by XRD from STADI P, STOE with CuK_α radiation from 0 to 100 (2θ) at room temperature. The morphology and microanalysis of the nanocomposites were studied by SEM (SEM-XL30, Philips). Varian UV–Vis spectrophotometer was used to determine the dye concentration.

2.4. Photocatalytic activity measurement

Photocatalytic dye decolorization experiments were carried out in a rectangular glass reactor with 1 L capacity. A 15 W UV-Lamp (Osram) was applied as a light source and it was placed in a quartz tube, which was installed inside the reactor (Fig. 1). Initially, 1 g of photocatalyst was added into a 1 L solution of MB with an initial concentration of 5 ppm. Before irradiation, the suspension was stirred for 24 h in darkness, due to elimination of absorption effect of the solution in the catalyst. After that, the lamp was switched on for starting the reaction. During irradiation, the suspensions were sampled at regular time intervals and immediately centrifuged to remove catalyst particles.

3. Results and discussion

3.1. FT-IR spectra

FT-IR spectra of the TiO_2/ZnO nanocomposite with different molar ratios of ZnO are shown in Fig. 2, in the wave number

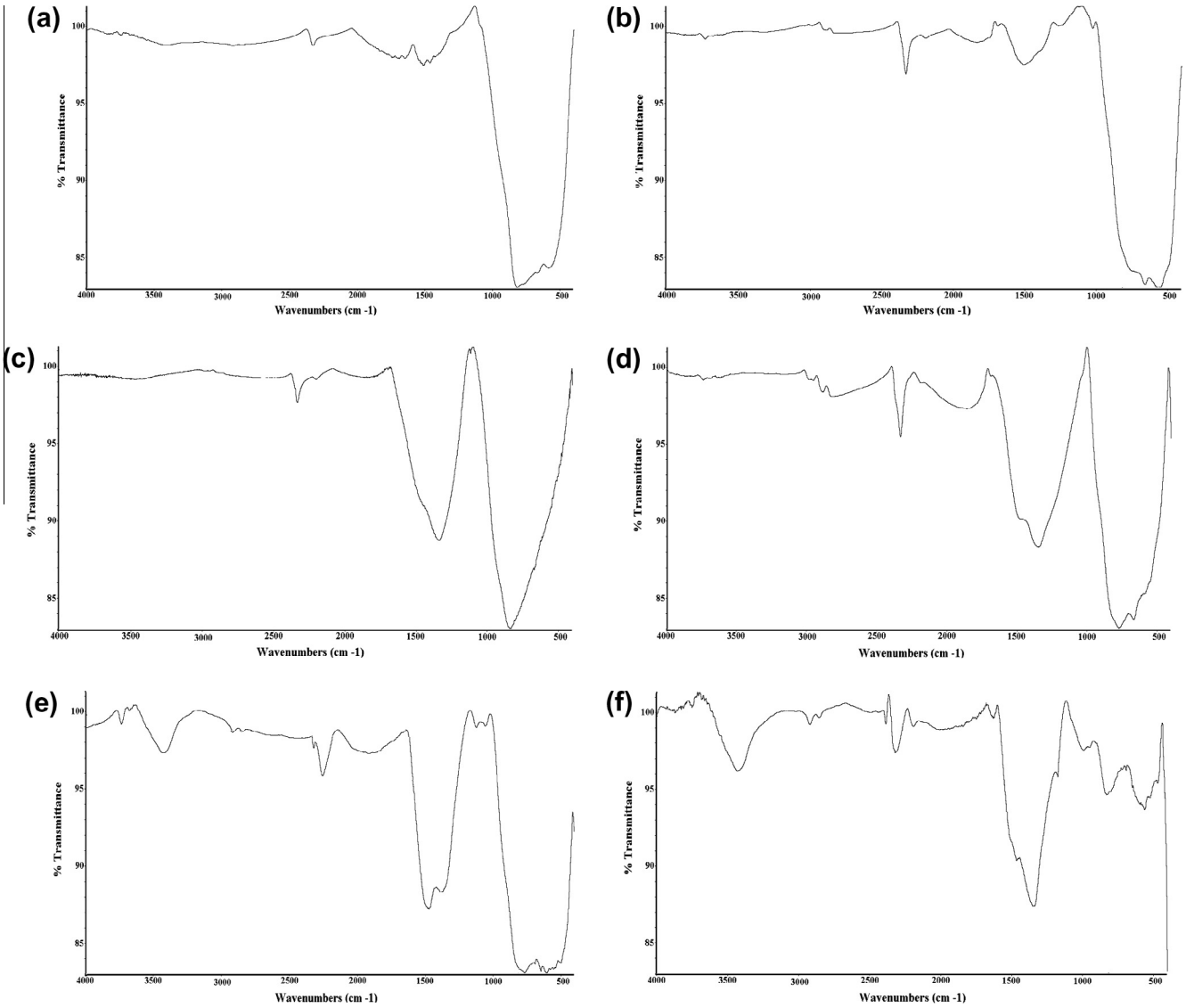

Figure 2 FT-IR spectra of powder samples. (a) Sample 1, (b) sample 2, (c) sample 3, (d) sample 4, (e) sample 5, (f) sample 6.

range from 4000 to 400 cm^{-1}. The peaks at 550 and 700 cm^{-1} can be assigned to symmetric stretching vibration of the Ti–O–Ti bond and O–Ti–O flexion vibration, respectively (Sava et al., 2007; Karthik et al., 2010). The peak intensities at 550 and 700 cm^{-1} were almost the same for samples 1–5, but strongly reduced in sample 6. The molar ratios of TiO_2 are the same in samples 1–5. In sample 6, further increasing of zinc oxide molar ratio until 15 decreases the O–Ti–O and Ti–O–Ti bonds formation thus the intensity of the peaks are reduced. The peaks at 800 cm^{-1} were attributed to the vibration mode of Zn–O–Ti (Wang et al., 2005b). The peaks at 400 and 1400 cm^{-1} were attributed to the vibration mode of Ti–O bond and all those at 1240, 1160 and 1080 cm^{-1} should be due to the Ti–OH bond. The peak at 1650 cm^{-1} resulted from the adsorbed H_2O molecules, which were not removed completely after sol–gel synthesis (Liao et al., 2006; Karthik et al., 2010). The wide peak at 3250 cm^{-1} has been assigned to the OH stretching vibration of surface hydroxyl group. During the hydrolysis of TTIP, large amount of ethanol lead to the appearance of hydroxyl bond (Aberomand Azar et al., 2010; Khodadadi et al., 2012).

3.2. SEM

Surface morphology of the synthesized nanocomposite has been studied and their SEM is shown in Fig. 3. Fig. 3a reveals TiO_2 nanoparticles which, synthesized from TTIP hydrolysis without adding any ZnO. It is seen that pure TiO_2 does not show a regular surface. They were irregularly shaped as aggregates due to the high viscosity of the sol, which reduced the dispersion of particles (Liao et al., 2008). Figs. 3b–f exhibit the TiO_2/ZnO nanocomposite at different molar ratios of ZnO. Through SEM, it was observed that the particle morphology of the TiO_2 was affected by the addition of ZnO and the size distribution of TiO_2/ZnO nanocomposite was improved with increasing ZnO molar ratio except sample 6. In samples 2–4, nanocomposites were composed of small agglomerates and nanoparticles (Abdel Aal et al., 2008; Tian et al., 2009a,b). In sample 5 with 50:10 M ratio of TiO_2/ZnO, regular morphology can be seen. It should be of interest for photocatalytic purposes since it expectantly improves the surface area (Rego et al., 2009). In sample 6, with further increases in ZnO molar ratio until 15, (TiO_2/ZnO; 50:15), some large aggregation with

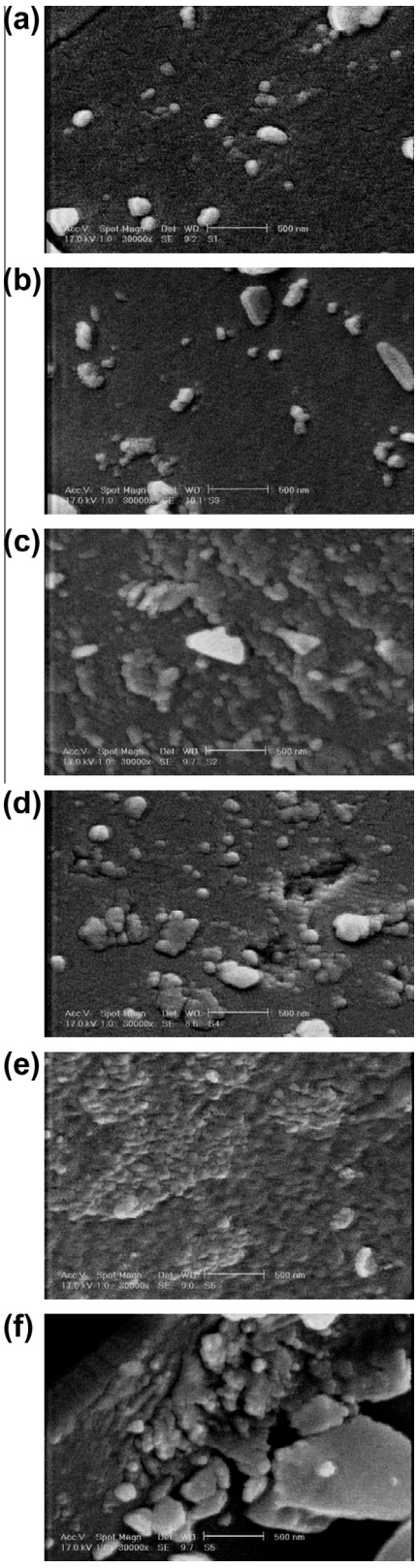

Figure 3 SEM images analysis of powder samples. (a) Sample 1, (b) sample 2, (c) sample 3. (d) sample 4, (e) sample 5, (f) sample 6.

different sizes were dispersed that decreased the photocatalytic activity.

Sample 5 reveals well ordered and good size distribution of particles and it was used for photocatalytic dye decolorization and showed no aggregation in comparison with other samples.

3.3. XRD

The XRD patterns of powders that were crystallized by using different molar ratios of TiO_2/ZnO from (50:0) to (50:15) is shown in Fig. 4. Six remarkable peaks were observed which related to anatase (25, 48), rutile (27), zincite (31, 47, 54, 57, 63, 67,69), zinc (43), titanium zinc oxide (40, 73) and titanium zinc phases (35) (Oyoshi et al., 2000; Wang et al., 2005a; Abdel Aal et al., 2008; Vaezi, 2008; Jiang et al., 2009). It can be seen anatase phase as the dominant phase is observed in all samples. In the sample 1, Fig. 4a, only anatase phase of TiO_2 was formed. Anatase phase solely does not show any good photocatalytic activity. After increasing the molar ratio of ZnO, in sample 2, Fig. 4b, three phases including, anatase, rutile, and zincite were exhibited. In this sample separate crystallization of TiO_2 and ZnO was observed. In samples 3 and 4, Fig. 4c and d, after increasing the molar ratio of zinc oxide, Ti and Zn were doped and the new phase called titanium zinc was formed with different molar ratios of Ti and Zn, ($Ti_{0.6}$ $Zn_{0.4}$) and (Ti Zn_3). In sample 5, Fig. 4e, separate crystallization of TiO_2 and ZnO was observed and with increasing the percentage of titanium and zincite phases, photocatalytic activity of samples has increased. In sample 6, Fig. 4f, a reaction between ZnO and TiO_2 to form Zn_2TiO_4 took place after further increase in the molar ratio of zinc oxide until 15 (TiO_2/ZnO; 50:15). The formation of photoinactive Zn_2TiO_4 decreases the photocatalytic activity (Wang et al., 2005a; Janitabar-Darzi and Mahjoub, 2009).

The crystallite size of samples 1–6 are estimated to be 72, 64, 56, 48, 37 and 92 nm, respectively, by using the sherrer equation

$$d = k\lambda/\beta\cos\theta$$

where β (radians) is the full-width of half maximum at 2θ 25.3, k is a constant (0.89), λ is the X-ray wavelength (0.1541 nm for Cu K_α), d is the particle diameter and θ is the angle of the diffraction peak (degrees) (Chan et al., 2009). The data revealed that TiO_2/ZnO molar ratio affected the particle size of nanocomposite. It is obvious that, in samples 1–5 with an increasing molar ratio of ZnO until 10 (TiO_2/ZnO; 50:10), the particle size decreased from 72 to 37 nm. Further addition of ZnO molar ratio until 15 (TiO_2/ZnO; 50:15), in sample 6, resulted in increasing the particle size until 92 nm due to the aggregation of particles.

3.4. Photocatalytic activity

Fig. 5 shows the effect of ZnO molar ratio on photodegradation of MB (5 ppm) in water under UV irradiation in a batch reactor at different time intervals.

According to Fig. 5, the photocatalytic activity enhances when ZnO molar ratio increases until 10 (TiO_2/ZnO; 50:10). In samples 1–5, absorbance of MB would be reached to 0 after 4, 4, 3.5, 3 and 2 h of irradiation. Sample 6, TiO_2/ZnO with 50:15 M ratio, showed the lowest photocatalytic activity and the MB degradation time increased to 4.5 h. Titanium dioxide is an effective photocatalyst that produces electrons and positive holes with UV irradiation. In the photocatalytic process,

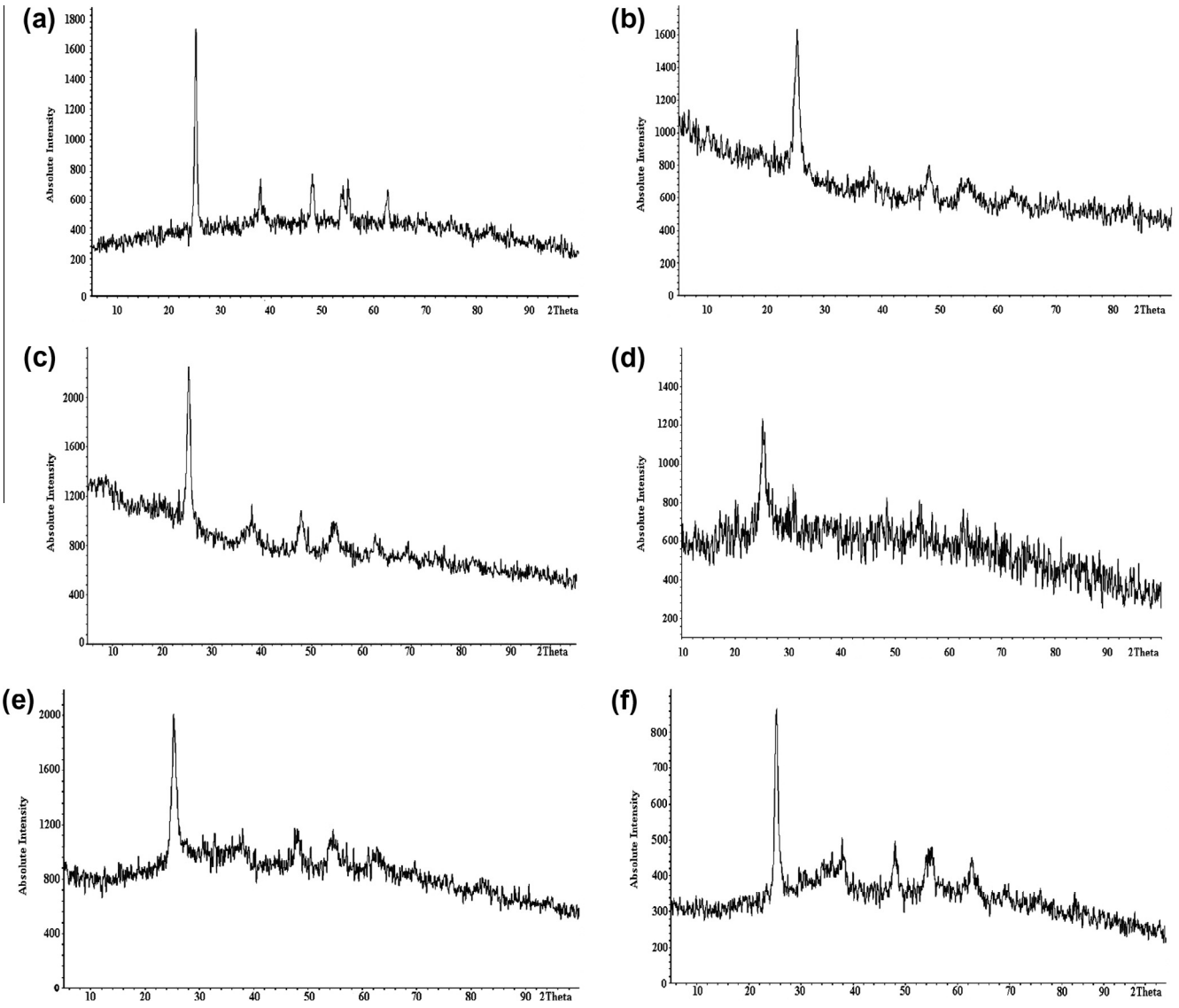

Figure 4 XRD patterns of powder samples. (a) Sample 1, (b) sample 2, (c) sample 3, (d) sample 4, (e) sample 5, (f) sample 6.

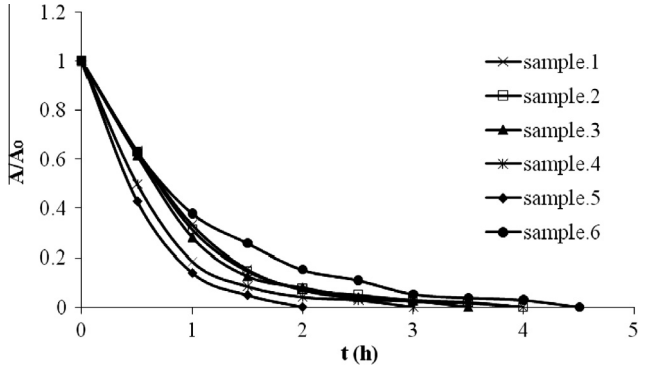

Figure 5 Decolorization of MB solution under UV radiation for powder samples.

TiO_2 semiconductor acts as a photocatalytic oxidation agent and a reductant. The generated electron–hole pairs in a photocatalytic process must be trapped in order to avoid recombination. The hydroxyl ions (OH^-) are the likely traps for holes, leading to the formation of hydroxyl radicals which are strong oxidant agents, while the traps for electrons are adsorbed oxygen species, leading to the formation of superoxide species (O^{2-}) which are unstable, reactive and may evolve in several ways. The degradation rate of pollutants are influenced by the active site and the photoabsorption of the catalyst used. Adequate loading of TiO_2/ZnO catalyst increases the generation rate of electron/hole pairs for enhancing the degradation of pollutants. However, addition of a high dose of the ZnO to TiO_2 decreases the light penetration by the photocatalyst suspension and reduces the degradation rate. This can be explained on the basis that the surface area is higher for smaller particles. Thus, increasing of ZnO ratio leads to decreasing the surface area and increasing the particle size of the catalyst. Catalyst sample with TiO_2/ZnO ratio of 50:10 has a crystalline and anatase form, which accelerates the catalytic efficiency (Barakat et al., 2004; Abdel Aal et al., 2008). In addition, the formation of photoinactive Zn_2TiO_4 at high ZnO ratio decreases the photocatalytic activity (Wang et al., 2005a; Janitabar-Darzi and Mahjoub, 2009).

Then Sample 5 has the best photocatalytic activity in comparison to other samples and the absorbance of MB solution has been reached to 0 after 2 h of irradiation.

4. Conclusions

The TiO_2/ZnO nanocomposite was prepared with different molar ratios of TiO_2/ZnO using the sol–gel method. The SEM images indicated that sample 5 reveals well ordered and good size distribution of particles and it was used for photocatalytic dye decolorization. In addition, sample 5 showed no aggregation in comparison with other samples. It is important for photocatalytic activity that the particle size of the photocatalyst should be homogeneous. The XRD study exhibited that in samples 1–5 with increasing the molar ratio of ZnO until 10 (TiO_2/ZnO; 50:10), the particle size decreased from 72 to 37 nm. Further addition of ZnO molar ratio until 15 (TiO_2/ZnO; 50:15, sample 6) resulted in increasing the particle size until 92 nm. The photocatalytic activity of the synthesized nanocomposite was investigated for decolorization of Methylene blue (MB). The results showed that after increasing the molar ratio of zinc oxide until 10 (TiO_2/ZnO; 50/10), the photocatalytic activity is enhanced gradually from sample 1–5. Addition of a high dose of ZnO to TiO_2 decreases the light penetration and reduces the degradation rate. So sample 5 has the best photocatalytic activity in comparison to other samples and the absorbance of MB solution has been reached to 0 after 2 h of irradiation.

References

Abdel Aal, A., Barakat, M.A., Mohamed, R.M., 2008. Electrophoresed Zn–TiO_2–ZnO nanocomposite coating films for photocatalytic degradation of 2-chlorophenol. Appl. Surf. Sci. 254, 4577–4583.

Aberomand Azar, P., Moradi Dehaghi, S., Samadi, S., Kamyar, S., Saber Tehrani, M., 2010. Effect comparison of Nd^{3+}, pectin and poly(ethylene glycol) on the photocatalytic activity of TiO_2/SiO_2 film. Asian J. Chem. 22, 1619–1627.

Barakat, M.A., Chen, Y.T., Huang, C.P., 2004. Removal of toxic cyanide and Cu(II) ions from water by illuminated TiO_2 catalyst. Appl. Catal. B-Environ. 53, 13–20.

Chan, C.C., Chang, C.C., Hsu, W.C., Wang, S.K., Lin, J., 2009. Photocatalytic activities of Pd-loaded mesoporous TiO_2 thin films. Chem. Eng. J. 152, 492–497.

Chen, C., Wang, Z., Ruan, S., Zou, B., Zhao, M., Wu, F., 2008. Photocatalytic degradation of C.I. acid orange 52 in the presence of Zn-doped TiO_2 prepared by a stearic acid gel method. Dyes Pigments 77, 204–209.

Chung, J.L., Chen, J.C., Tseng, C.J., 2008. Electrical and optical properties of TiO_2-doped ZnO films prepared by radio-frequency magnetron sputtering. J. Phys. Chem. Solids 69, 535–539.

Janitabar-Darzi, S., Mahjoub, A.R., 2009. Investigation of phase transformations and photocatalytic properties of sol–gel prepared nanostructured ZnO/TiO_2 composite. J. Alloys Compd. 486, 805–808.

Jiang, Y., Wu, M., Wu, X., Sun, Y., Yin, H., 2009. Low-temperature hydrothermal synthesis of flower-like ZnO microstructure and nanorod array on nanoporous TiO_2 film. Mater. Lett. 63, 275–278.

Karthik, K., Kesava Pandian, S., Victor Jaya, N., 2010. Effect of nickel doping on structural, optical and electrical properties of TiO_2 nanoparticles by sol–gel method. Appl. Surf. Sci. 256, 6829–6833.

Khan, R., Kim, T.J., 2009. Preparation and application of visible-light-responsive Ni-doped and SnO_2-coupled TiO_2 nanocomposite photocatalysts. J. Hazard. Mater. 163, 1179–1184.

Khan, R., Kim, S.W., Kim, T.J., 2008. Synthesis and control of physical properties of Titania nanoparticles as a function of synthetic parameters. J. Nanosci. Nanotechnol. 8, 4738–4742.

Khodadadi, B., Sabeti, M., Moradi, S., Aberomand Azar, P., Raeis Farshid, S., 2012. Synthesis of Cu–TiO_2 nanocomposite and investigation of the effectiveness of PEG, pectin, and CMC as additives. J. Appl. Chem. Res. 20, 36-34.

Kim, K.E., Jang, S.R., Park, J., Vittal, R., Kim, K.J., 2007. Enhancement in the performance of dye-sensitized solar cells containing ZnO-covered TiO_2 electrodes prepared by thermal chemical vapor deposition. Sol. Energ. Mater. Sol. C 91, 366–370.

Liao, D.L., Badour, C.A., Liao, B.Q., 2008. Preparation of nanosized TiO_2/ZnO composite catalyst and its photocatalytic activity for degradation of methyl orange. J. Photochem. Photobiol. A 194, 11–19.

Liao, S., Donggen, H., Yu, D., Su, Y., Yuan, G., 2004. Preparation and characterization of ZnO/TiO_2, SO_4^{2-}/ZnO/TiO_2 photocatalyst and their photocatalysis. J. Photochem. Photobiol. A 168, 7–13.

Liao, M.H., Hsu, C.H., Chen, D.H., 2006. Preparation and properties of amorphous titania-coated zinc oxide nanoparticles. J. Solid State Chem. 179, 2020–2026.

Liqiang, J., Baifu, X., Fulong, Y., Baiqi, W., Keying, S., Weimin, C., Honggang, F., 2004. Deactivation and regeneration of ZnO and TiO_2 nanoparticles in the gas phase photocatalytic oxidation of *n*-C_7H_{16} or SO_2. Appl. Catal. A-Gen. 275, 49–54.

Miki-Yoshida, M., Collins-Martinez, V., Amezaga-Madrid, P., Aguilar-Elguezabal, A., 2002. Thin films of photocatalytic TiO_2 and ZnO deposited inside a tubing by spray pyrolysis. Thin Solid Films 419, 60–64.

Oyoshi, K., Sumi, N., Umezu, I., Souda, R., Yamazaki, A., Haneda, H., Mitsuhashi, T., 2000. Structure, optical absorption and electronic states of Zn^+ ion implanted and subsequently annealed sol–gel anatase TiO_2 films. Nucl. Instrum. Meth. B 168, 221–228.

Rego, E., Marto, J., São Marcos, P., Labrincha, J.A., 2009. Decolouration of Orange II solutions by TiO_2 and ZnO active layers screen-printed on ceramic tiles under sunlight irradiation. Appl. Catal. A-Gen. 355, 109–114.

San, N., Hatipoglu, A., Kocturk, G., Cinar, Z., 2002. Photocatalytic degradation of 4-nitrophenol in aqueous TiO_2 suspensions: theoretical prediction of the intermediates. J. Photochem. Photobiol., A 146, 189–197.

Sava, B.A., Diaconu, A., Elisa, M., Grigorescu, C.E.A., Vasiliu, C., Manea, A., 2007. Structural characterization of the sol–gel oxide powders from the ZnO–TiO_2–SiO_2 system. Superlattices Microst. 42, 314–321.

Siemon, U., Bahnemann, D., Testa, J.J., Rodriguez, D., Litter, M.I., Bruno, N., 2002. Heterogeneous photocatalytic reactions comparing TiO_2 and Pt/TiO_2. J. Photochem. Photobiol. A 148, 247–255.

Tian, J., Chen, L., Dai, J., Wang, X., Yin, Y., Wu, P., 2009a. Preparation and characterization of TiO_2, ZnO, and TiO_2/ZnO nanofilms via sol–gel process. Ceram. Int. 35, 2261–2270.

Tian, J., Chen, L., Yin, Y., Wang, X., Dai, J., Zhu, Z., Liu, X., Wu, P., 2009b. Photocatalyst of TiO_2/ZnO nano composite film: preparation, characterization, and photodegradation activity of methyl orange. Surf. Coat Tech. 204, 205–214.

Vaezi, M.R., 2008. Two-step solochemical synthesis of ZnO/TiO_2 nano-composite materials. J. Mater. Process Tech. 205, 332–337.

Wang, C., Xu, B.Q., Wang, X., Zhao, J., 2005a. Preparation and photocatalytic activity of ZnO/TiO_2/SnO_2 mixture. J. Solid State Chem. 178, 3500–3506.

Wang, X.T., Zhong, S.H., Xiao, X.F., 2005b. Photo-catalysis of ethane and carbon dioxide to produce hydrocarbon oxygenates over ZnO-TiO_2/SiO_2 catalyst. J. Mol. Catal. A-Chem. 229, 87–93.

Weber, E.J., Stickney, V.C., 1993. Hydrolysis kinetics of reactive blue 19-vinyl sulfone. Water Res. 27, 63–67.

Xie, Y., Yuan, C., 2004. Characterization and photocatalysis of Eu^{3+}–TiO_2 sol in the hydrosol reaction system. Mater. Res. Bull. 39, 533–543.

Zhang, Z., Yuan, Y., Fang, Y., Liang, L., Ding, H., Jin, L., 2007. Preparation of photocatalytic nano-ZnO/TiO_2 film and application for determination of chemical oxygen demand. Talanta 73, 523–528.